# MICROFLUIDIC SIEVE USING INTERTWINED, FREE-STANDING CARBON NANOTUBE MESH AS ACTIVE MEDIUM

BY

Olgica Bakajin                    (Serbia & Montenegro)
16091 Gramercy
San Leandro, Ca 94578

Aleksandr Noy                     (USA)
2411 Cipriani Blvd.
Belmont, CA 94002

# MICROFLUIDIC SIEVE USING INTERTWINED, FREE-STANDING CARBON NANOTUBE MESH AS ACTIVE MEDIUM

[0001] The United States Government has rights in this invention pursuant to Contract No. W-7405-ENG-48 between the United States Department of Energy and the University of California for the operation of Lawrence Livermore National Laboratory.

## I. CLAIM OF PRIORITY IN PROVISIONAL APPLICATION

[0002] This application claims priority in provisional application filed on July 3, 2002, entitled "Microfabricated Channel with Patterned Carbon Nanotube Array Active Element and a Fabrication Strategy for such Device" serial number 60/393,425, by inventors Bakajin et al.

## II. FIELD OF THE INVENTION

[0003] The present invention relates to molecular and chromatographic separation mediums, and more particularly to a microfluidic sieve utilizing an intertwined free-standing carbon nanotube mesh as an active medium in a microfluidic channel for separating, concentrating, and/or filtering molecules flowed therethrough.

## III. BACKGROUND OF THE INVENTION

[0004] The advantages and benefits of using microfluidic separation elements and devices utilized in, for example, HPLC-on-a-chip systems and gas chromatography systems, are generally well known. In many cases, such systems are fabricated using microfabrication techniques similar to those employed in the manufacture of computer

chips. Such techniques bring to on-chip molecular separation systems many of the same benefits as computer chip fabrication, such as faster processing speed, increased throughput, multiplexing, and cost savings. It also enables the development of molecular and chromatographic analytical systems and methods requiring with very low sample consumption.

[0005] Microfabricated fluidic systems are also being developed which employ nano-scale arrays comprising carbon nanotubes or other nanofeatures for use as separation matrices. One such example, utilizes nano-scale arrays of silicon pillars as separation matrices. However, the lithographic process at the nano-scale has been extremely difficult in the past. Other complications found in other on-chip separation device developments include, for example, the packing of columns with silica beads, which can complicate the fabrication process and drive up cost. Even highly efficient microfabricated devices such as those used for gas separation, still require that their columns be packed with carbon. If the packing process could be avoided, the microfabricated devices can be made more complex and more integrated.

[0006] One example which avoids the packing process is disclosed in the PCT publication number WO 01/63273 A2 to Noca et al, describing a molecular sieve employing self-assembled nano-arrays to separate molecules by differential transport therethrough via electrophoresis. The nano-arrays are fabricated using a template having germination points from which the nano-arrays are grown. As shown in the drawings, however, the template produces nano-features of uniform straightness and length which all have the same or similar orientations not intertwined or entangled with respect to each other. The "pores" in the Noca publication, therefore, are effectively defined by the

3

spacing of the nano-features. While the Noca separation device is utilized to separate DNA strands traveling at different velocities through the device, the pore construction would be unable to also perform concentration or filtration functions effectively due to its large vertical pores that span the depth of the channel.

[0007] It would be advantageous, therefore, to provide a simple microfluidic sieve device which avoids the need to pack beads, and which also utilizes nanofeatures, i.e. carbon nanotubes, grown into an intertwined mesh to serve as an active medium for separating, concentrating, and/or filtering molecules.

## IV. SUMMARY OF THE INVENTION

[0008] One aspect of the present invention includes a microfluidic sieve comprising: a substrate having a microfluidic channel; and a carbon nanotube mesh comprising a plurality of intertwined free-standing carbon nanotubes fixedly attached within said channel for separating, concentrating, and/or filtering molecules flowed therethrough.

[0009] Another aspect of the present invention includes a method of fabricating a microfluidic sieve, comprising: providing a substrate having a microfluidic channel; and growing a plurality of intertwined free-standing carbon nanotubes in said channel to produce a carbon nanotube mesh fixedly attached therein and capable of separating, concentrating, and/or filtering molecules flowed therethrough.

[0010] And another aspect of the present invention includes a method of separating, concentrating, and/or filtering molecules comprising: flowing said molecules through a microfluidic channel having a carbon nanotube mesh comprising a plurality of intertwined free-standing carbon nanotubes fixedly attached within said channel, whereby

4

said carbon nanotube mesh operates as an active medium for separating, concentrating, and/or filtering said molecules.

## V. BRIEF DESCRIPTION OF THE DRAWINGS

[0011] The accompanying drawings, which are incorporated into and form a part of the disclosure, are as follows:

[0012] Figure 1A is a schematic cross-sectional view of a first exemplary embodiment of the present invention illustrating the deposition of a catalyst in a microfluidic channel.

[0013] Figure 1B is a schematic cross-sectional view following Figure 1A, illustrating an oxidation stage of fabrication.

[0014] Figure 1C is a schematic cross-sectional view following Figure 1B, illustrating a carbon nanotube growth stage of fabrication.

[0015] Figure 1D is a schematic cross-sectional view following Figure 1C, illustrating a capping stage of fabrication and the completed structure with a carbon nanotube mesh completely filling the channel.

[0016] Figure 2 is a schematic cross-sectional view of a second exemplary embodiment of the present invention, having a carbon nanotube mesh surface-coating the channel walls.

[0017] Figure 3 is a schematic perspective view of an illustrative flow of molecules through the microfluidic sieve of the present invention.

[0018] Figure 4 is a schematic perspective view of an illustrative flow of molecules similar to Figure 3 but shown with a microfluidic sieve having two microfluidic channels with varying mesh arrangements.

5

[0019] Figure 5 is an image of a carbon nanotube mesh grown inside a microfabricated channel, and shown without a channel cover.

[0020] Figure 6 is a magnified image of a carbon nanotube mesh grown according to the method of the present invention.

[0021] Figure 7 is a magnified image of a microfluidic channel with a curved cross-section and a carbon nanotube mesh growth therein.

[0022] Figure 8 is a magnified image of a carbon nanotube mesh having fluorescent beads adsorbed thereon as a result of surface functionalization.


## VI.  DETAILED DESCRIPTION

[0023] The present invention is directed to a microfluidic sieve utilizing a mesh of intertwined free-standing carbon nanotubes grown within a microfluidic channel of a substrate to provide any one or more or all of separation, concentration, and/or filtering functions with respect to molecules and analytes present in a fluid flow (i.e. gas or liquid flow).  The unique properties of carbon nanotubes, such as its small, tunable dimensions, e.g. pore size, a large surface-to-volume ratio (greater than packed bead columns), modifiable surface properties, etc., provide many advantages when used with microfluidic sieves for separation and concentration functions in various chromatographic applications.  The present invention utilizes these unique properties of carbon nanotubes by growing a plurality of intertwined free-standing carbon nanotubes to attach within a microfluidic channel which is subsequently sealed.  The mesh may be grown to completely fill a segment of the channel, i.e. its cross-section is filled, or grown

6

to surface-coat a segment of the channel without completely filling the segment, so as to produce a gap through the segment.

[0024] It is notable that separation, concentration, and filtration operations are related if not similar operations involving the discrimination and/or selection of molecules based on a molecular property or properties, such as structural properties of size, weight, etc., chemical properties, e.g. hydrophilic, hydrophobic, etc., and even electrical properties having positive or negative charge. It is appreciated, however, that concentration and filtration further suggest that particles, i.e. molecules, are selectively retained after being separated. In this regard, and depending on the application, the microfluidic sieve of the present invention may actively operate to achieve any one or more or all of these functions, without being limited to any one.

[0025] While various fabrication methods may be employed for fabricating the microfluidic sieve of the present invention, the preferred fabrication method of the present invention uses chemical vapor deposition (CVD) employing a CVD growth catalyst. And preferably the catalyst for use in a CVD growth process nanotube growth is metallic iron (Fe). Applicants have been able to demonstrate that iron colloids supported on alumina nanoparticles, iron colloids alone, and thin layers of iron all lead to sufficient nanotube growth. In all cases, a high-temperature CVD reactor is utilized to effect pyrolysis of a reactant mixture, with the carbon nanotubes being grown by passing the hydrocarbon pyrolysis products over the iron catalyst. For a thin film iron layer of about 5 nanometers, a mixture of ethylene, hydrogen, and argon may be pyrolized at about 800-850 degrees Celsius. After growing the carbon nanotube mesh, the microfluidic channel may be sealably enclosed and capped with a cover, such as a glass

7

cover slip, to contain and pack the mesh therein. The surfaces of the nanotube mesh may also be functionalized to select/discriminate molecules as required by the application.

[0026] Turning now to the drawings, Figures 1A-D show the fabrication of a first embodiment of the microfludic sieve, generally indicated at reference character 10 (in Figure 1D) using a CVD growth process. As shown in Figure 1A, a channel 11 is first formed, e.g. by etching a groove, in a substrate made of silicon, fused silica or other patternable material. While a grooved channel configuration is shown having a floor surface and opposing vertical sidewall surfaces, it is appreciated that the channel and its cross-section may be configured with any suitable geometry, such as the curved cross-section shown in Figure 7. Next a layer of iron catalyst 12 is deposited in the channel 11. The layer of iron catalyst is preferably a thin film layer having a thickness of about 5 nanometers, and deposited using thin film deposition techniques, such as evaporation or sputtering, with lithographic masking. It is appreciated, that as an alternative to an iron layer, colloidal iron nanoparticles and iron nanoparticles supported on the fumed alumina surface may be utilized to grow carbon nanotubes as well.

[0027] Figure 1B shows the deposited layer of Figure 1A then converted into iron oxide 13 by heating the substrate in an oxygen furnace, such as at 300 degrees Celsius for about 5 hours. The iron oxide is then reduced back into metallic iron by heating it in the hydrogen-rich atmosphere.

[0028] As shown in Figure 1C, carbon nanotubes are then grown in the channel to produce an intertwined free-standing carbon nanotube mesh 14. The mesh is produced by passing products of hydrocarbon pyrolysis over the catalyst surface at elevated temperatures, e.g. above 800 degrees Celsius. Structural mesh parameters of height,

density, and pore size are regulated mostly by the density and size parameters of the nanotubes. Both of these parameters are controllable by changing gas flows, flow ratios, and catalyst thickness. The grown carbon nanotube mesh 14 has pores of variable and tunable size on the order of 10-200 nanometers. The resulting mesh is stable in a variety of organic solvents and in air due to the nanotubes being chemically inert, and resists ultrasonication very well. Furthermore, carbon nanotube elements possess unique mechanical strength and elasticity which makes the mesh highly robust.

[0029] It is notable that because the carbon nanotubes consist of a mesh of the carbon nanotubes grown directly from solid or porous support of the channel surface, they are free-standing features supported by the channel. Moreover, the nanotubes extend randomly from this support into free space, e.g. the channel volume, characteristic of a free-grown structure to form a dense intertwined and entangled mesh as shown in Figures 5-7. Carbon nanotube meshs can be grown in this fashion over extended macroscopic surfaces, on lithographically defined microscale areas and inside microfabricated structures, such as the microfluidic channel 14. Moreover, the carbon nanotubes produced in this manner conforms to the shape of the microfluidic channel as shown in the figures. Since Fe catalyst can be easily patterned using standard lithographic techniques, nanotube meshs are easily patternable for applications that require miniaturization and integration of devices, such as for specific parts of a microfabricated device. Carbon nanotube meshs may be tuned to a particular application since it is possible to control nanotube size, density and orientation in the growth process.

[0030] Additionally, the carbon nanotube mesh of the present invention may be further customized by functionalizing the surface properties of the nanotubes to select and/or

discriminate molecules. Surface functionalization may be achieved, for example, by applying different nanotube coatings and derivatizations of specific chemical groups. The coatings may be polymers or small molecules that either incorporate particular chemical functionality or facilitate the chemical attachment of a functionality. Figure 8 shows a magnified view of a functionalized carbon nanotube mesh of the present invention with having fluorescent beads adsorbed thereon as a result of surface functionalization.

[0031] Figure 1D follows from Figure 1C to show sealing of the channel with a cover 15 to enclose the nanotubes therein. In particular, and after the mesh is grown, the channel is enclosed by bonding the cover 15 to the substrate containing the mesh and capping the channel. The bonding procedure typically uses anodic bonding of a Pyrex cover slip to the top surface of the substrate, or fusion bonding of fused silica. Because of the nanotubes, this is typically performed under vacuum or in an inert atmosphere. As can be seen from Figures 1C and 1D, the cover 15 is utilized to pack the outgrowth of the mesh from the channel. This is made possible by growing the nanotubes a bit higher than the channel wall size, as shown in Figure 1C, and then we packing the mesh as the channel is sealed. In this manner, a good contact may be formed without producing a gap between the mesh and the cover.

[0032] Figure 2 shows a second embodiment of the microfluidic sieve, generally indicated at reference character 20, wherein the carbon nanotube mesh 23 is surface-coated along the channel without filling the cross-section of the channel. In particular, the mesh 23 is surface coated along all sides of the channel, including the channel sidewalls 21 and the channel floor 22. In this manner, a gap 24 is formed through the

10

mesh 23 and the channel, whereby flow may continue for certain applications, while

target molecules or analytes are separated, concentrated and/or filtered in the mesh 23.

The cover 25 is shown without the mesh surface-coated thereon, because, as previously

discusse, the cover is typically bonded subsequent mesh growth within the channel.

However, in this embodiment as well, the cover 25 may serve to pack any outgrowth of

nanotubes along the top edge back within the channel.

[0033] Operation and use of the microfluidic sieve is shown in Figures 3 and 4. Figure 3

shows a single channel embodiment 30 having a single carbon nanotube mesh 32 therein,

and Figure 4 shows a double channel embodiment 40 having varying mesh arrangements.

As shown in Figure 3, the mesh 32 is grown and fixedly attached to at least a segment of

the channel 31, where the segment may be the entire channel or a portion thereof.

Arrows are shown indicating the flow direction of a fluid containing molecules 33. It is

appreciated that the sieve may used for separating, concentrating, and/or filtering either

gas mixtures or liquid solutions containing organic, inorganic, and biological species. In

contrast to Figure 3, the sieve 40 of Figure 4 has a first channel 41 having a single mesh

42 fixedly attached therein, and a second channel 43 having a first mesh 44 fixedly

attached to the channel, and a second mesh 45 also attached to the channel at an upstream

location with respect to the first mesh 44. The first and second meshes are located at

corresponding segments of the channel, wherein each segment is less than the entire

length of the channel. With this arrangement, the meshes 44 and 45 may be configured,

as discussed above, such that the sieve operates to optimally separate, concentrate, and/or

filter molecules flowed therethrough.

[0034] As shown in Figure 5, a securing nubbin, such as a lithographically formed post, may be positioned in the channel to prevent the dislocation of said carbon nanotube mesh, in the case where the mesh breaks away from its attachment to the channel. Preferably, the microfabricated post is positioned downstream of and adjacent to said carbon nanotube mesh.

[0035] While operation of the microfluidic sieve of the present invention may be intended for separation applications, such as electrophoretic separtion, it is not limited only to such. The present invention may be utilized with pressure driven flow for other applications, such as, but not limited to: size exclusion chromatography (filtering); use as chromatography media (gas or liquid) by exploiting the different sticking probability of different chemical species to surfaces of bare nanotubes and modified nanotubes; and as concentrators for concentrating species by accumulating them either at the front boundary or just along the nanotube element, and subsequently releasing the collected species by changing environmental conditions to recover concentrated substrate. CNT as a patternable separation medium, therefore, may be utilized for various applications. Example applications, include but not limited to: gas chromatography, size exclusion liquid chromatography in a solvent that wets carbon nanotubes, filtering and concentration, possible HPLC-type separation or selective adsorption for molecules that have natural affinity to the aromatic graphite-like structure of nanotubes (dioxins are just one example). Furthermore, microfluidic sieves having a derivatized carbon nanotube mesh may be utilized, for example, for more targeted gas chromatography; size exclusion liquid chromatography in a water based solvent; filtering and concentration; separation of proteins (similar to RP HPLC); and DNA separations via electrophoresys.

[0036] While particular operational sequences, materials, temperatures, parameters, and particular embodiments have been described and or illustrated, such are not intended to be limiting. Modifications and changes may become apparent to those skilled in the art, and it is intended that the invention be limited only by the scope of the appended claims.